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Hide unhairing: Achieving lower pollution loads, decreased wastewater toxicity and solid waste reduction

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Abstract

This study aims to diminish the pollution being discharged into wastewaters through changes in the unhairing process. To this aim, we are replacing a reductive hair degrading process with a process which combines a reductive hair degrading process with an oxidative hair degrading process. Hydrogen peroxide is used to decrease the supply of sulfide as unhairing chemical. As a result, commercially acceptable leather regarding both costs and quality is obtained and significant reductions in the contaminant load of the wastewater being discharged are observed. Results indicate that wastewater conductivity is

cut by 26%, suspended solids decrease by 75%, observable sulfide disappears, while the amount of chromium being absorbed by the hides is increased. This leads to considerable savings in the chromium salt offer in hide tanning and, consequently, a decrease in the amount chromium in the wastewater.

Keywords: Unhairing; Tanning; Leather; Hydrogen peroxide; Pollution reduction

1. Introduction

Chemically speaking, tanning means stabilizing a protein called collagen, which is the main constituent of the skin. The tanning process may be divided into several stages. The beamhouse procedures are cleaning operations that prepare the hides for the subsequent leather making process. Beamhouse involves high water consumption and is considered as highly polluting. Actually, this is the stage that generates the most polluted wastewaters (Saravanabhan et al., 2006) and most solid waste (Kanagaraj et al., 2015). According to data published by the International Union of Leather Technologists and Chemists Societies (IULTCS, 2008), the beamhouse stage uses about 60% of all the water consumed in the whole tanning process and generates about 75% of the chemical oxygen demand (COD), 80% of suspended solids (SS), and 100% of sulfide (S^{2-}).

These data are an average assuming good practices in working conditions. According to the Food and Agriculture Organization of the United Nations (FAO, 2013), yearly world production of cattle hides, expressed in wet salted weight, approaches 6.5 Mt. This means that each year beamhouse operations worldwide approximately consume 104

Mm^3 of water. Likewise, approximately 0.91 Mt of COD, 0.036 Mt SS and 0.62 Mt of S^{2-} are generated. These figures are actually lower than the real ones especially for two reasons. First, numerous tanneries are located in countries where environmental laws are practically nonexistent, which suggests that the import figures are actually higher. Second, besides tanned cowhides, also other types of skins are being tanned worldwide (sheep, pigs, reptiles, etc.), although to a much lesser extent. In fact, cowhides account for approximately 75% of total world leather. All in all, the figures above suggest that the pollution generated during the beamhouse stage may be considered a major environmental problem.

Unhairing, one of the operations during the beamhouse stage, consists in removing the hair or wool off the hides and skins. The reagents conventionally being used during this operation are sodium sulfide and/or sodium hydrosulfide and lime. After a reductive reaction, the joint action of hydrosulfide (HS^-) and hydroxyl (OH^-) ions causes the disruption of the disulfide bridges of hair cystine, thus transforming it into cysteine and obtaining the subsequent hydrolysis of keratin (hair protein). *Eq. (1)* shows one of the possible mechanisms of this reaction.

$$\text{-S-S-} + 2\ ^-\text{SR} \rightarrow \text{-S-S-R} + \text{R-S-S-} \qquad (1)$$

The hydrolysis of keratin influences the characteristics of the effluent resulting from the unhairing process, and therefore its COD and Total Kjeldahl Nitrogen (TKN) values are considerably high. The presence of hydrosulfide and sulfide ions is also a major challenge, especially due to the possibility of transformation into hydrogen sulfide (Black et al., 2013). Over the years there have been numerous poisonings and even fatalities due to inhalation of hydrogen sulfide. Theoretically, hydrogen sulfide production should be avoided by maintaining the pH of the float at a certain level, as the chemical reaction below shows in *Eq. (2)*.

$HS^- + H_2O \leftrightarrow H_2S\uparrow + OH^-$ *(2)*

Unfortunately though, production of hydrogen sulfide has not always been avoided. Besides, sulfide and hydrosulfide ions are not completely removed from the hides, which is also major drawback. The next step after unhairing is the fleshing operation, in which a large amount of solid waste is generated. The fleshings contain sulfides and this increases the difficulty and cost of their recovery for glue, gelatin or cosmetic production (Bayramoglu et al., 2014).

In the last decades numerous studies (Vidal et al., 2004; Sengil et al., 2009; Haydar and Aziz, 2009) have been carried out to try to minimize the environmental impact of unhairing. One of the systems to reduce pollutant loads from residual floats and thus facilitate their subsequent treatment is to implement the hair recovery process (Frendrup, 2000; Valeika et al., 2009; Galarza et al., 2010). This process consists of two parts: First the shaft of the hair is protected with lime against the attack of sodium sulfide. This operation is called immunization and involves the formation of compounds such as lanthionine (see Fig. 1) and other similar compounds. As a result, only the hair root undergoes hydrolyzation, whereas the shaft of the hair separates from the hide without hydrolyzing, and COD and TKN values are significantly reduced in the wastewater float. Subsequently, the hair root must be hydrolyzed by adding more sodium sulfide. This system is used on an industrial scale and its main problem is the presence of sulfides in waste floats and in unhaired hides.

Another line of research is based on the use of hydrogen peroxide as an unhairing agent instead of sodium sulfide/hydrosulfide (Bronco et al., 2005; Morera et al., 2008; Andrioli and Gutterres, 2014). Hydrogen peroxide, at pH values close to 13, is capable of

hydrolyzing the hair through an oxidative reaction. The oxidative attack of the S-S bond is due to the formation of peroxy anion from hydrogen peroxide (*Eq. (3)*).

$H_2O_2 \leftrightarrow HOO^- + H^+$ *(3)*

Research has also been conducted to explore the possibility of performing this type of unhairing by immunizing the hair first in order to minimize the pollution load from wastewater floats. The environmental impact of this practice has been evaluated by performing a life cycle assessment (LCA) (Castiello et al., 2006). This system reduces the pollution discharged and eliminates sulfides in the wastewater. However, further research is needed to implement it in the industry.

The use of enzyme products to replace sodium sulfide as an unhairing agent is an old practice (Heidemann, 1993). The problem is that the enzymes used to date, besides attacking the hair, do also attack the collagen, thus damaging the surface of the hides. Of course, this considerably diminishes the commercial value of hides and therefore is an impediment to the industrial application of this system. However, numerous researchers are currently exploring the behavior of various unhairing enzymes on the hides under different conditions of pH, temperature, concentration, etc. (Thangam et al., 2001; Jian et al., 2011; Dettmer et al., 2012).

In short, there are various lines of research open to explore the replacement of sodium sulfide as unhairing agent. So far though, an effective, inexpensive product that may be applied at an industrial scale has not yet been found.

Our work has studied the possibility of modifying the reductive unhairing process with hair recovery (using lime, sodium sulfide and sodium hydrosulfide), combining it with an oxidative unhairing (using hydrogen peroxide) to obtain less polluted wastewater. Moreover, the new process is less toxic due to sulfide removal.

Specifically our studies aim to eliminate the use of sodium sulfide to hydrolyze the hair root, replacing it with hydrogen peroxide, as well as examine the consequences of this change in the discharged wastewater. The anticipated improvement in wastewater quality should not compromise the physical properties of the leather required for the manufacture of consumer goods.

2. Materials and methods

2.1. Materials

Part of the laboratory tests were carried out using 0.40 m in diameter and 0.15 m wide stainless steel drums, Inoxvic brand. The rest of the laboratory tests and the pilot plan tests were carried out using 1 m in diameter and 0.4 m wide stainless steel drums, Olcina brand. Drums are cylindrical vessels that rotate around an axle (Fig. 2).

The chemicals and the machinery used in the beamhouse operations were those normally used in the leather industry: Sodium hydroxide (50% w/w), lime (95% w/w), sodium hydrosulfide (70% w/w), sodium sulfide (60% w/w), formic acid (85% w/w) and ammonium sulfate (99% w/w). The bating agent is a commercial product based on proteatic enzymes. Provided by TFL its name is Oropon OR. The unhairing auxiliary is a commercial product that is based on secondary amines and has unhairing properties. Provided by Cromogenia Units S.A. its name is Ribersal PLE BASE. For laboratory analysis grade chemicals were used.

Soaked and fleshed bovine hides were used in order to perform the tests.

2.2. Methodology

All tests were conducted in triplicate.

The experimentation was performed in two stages, namely laboratory and pilot plant, which will be detailed below.

2.2.1. Laboratory tests.

The objective of these tests was to determine the amount of hydrogen peroxide required to remove the hair roots with the same efficiency as the traditional method, based on the use of sodium sulfide and / or hydrosulfide.

Three soaked and fleshed bovine salted hides were used to perform the tests. The first part of the reductive unhairing was performed following the traditional formula (Table 1).

Table 1

Laboratory tests: Reductive unhairing formula (first part)

100% Water	T = 30 ºC
0.5% Sodium hydroxide (50%)	Rotate 10 min.
1% Amine product	Rotate 1 h. pH = 10
0.8% Lime	Rotate 30 min.
1% Sodium hydrosulfide	Rotate 30 min.
1% Sodium sulfide	Rotate 8 h. Overnight rest
	Rotate 2h.
Wash twice	

Rest 24 h. on a horse

Subsequently, five pieces of approximately 0.1 m x 0.5 m were cut from each hide. The pieces were cut from the center of the hide to establish comparative tests. The pieces were then subjected to treatment with hydrogen peroxide (oxidative unhairing) to remove hair roots that remained in the skin. Each piece was processed separately, thus varying the offers of hydrogen peroxide. Offers of sodium hydroxide and formic acid were also varied to maintain the appropriate pH of the skin at all times. Table 2 shows the formula of oxidative unhairing, while Table 3 outlines the various offers tested on the chemicals.

Table 2

Laboratory tests: Oxidative unhairing formula

30% Water	T = 25 ºC
0.5% Sodium hydroxide (50%)	Rotate 15 min.; pH =13
X/2% Hydrogen peroxide (50%)	Rotate 15 min.
Y% Sodium hydroxide	Rotate 15 min.
X/2% Hydrogen peroxide (50%)	Rotate 2 h.
Z% Formic acid	In three times. Rotate 45 min.
170% Water	Rotate 3.5h. Night: Rotate 5 min. per hour.
	pH = 8.7
Drain and wash the hide	

Table 3

Offer of chemicals for each laboratory test

Test	Hydrogen peroxide (X%)	Sodium hydroxide (Y%)	Formic acid (Z%)
1	4.5	4	2
2	3	2	1.5
3	2.5	1.67	1.4
4	2	1.33	1.3
5	1	0	0.5

After completing all the oxidative unhairing tests, cuts were made in each piece of hide and the pieces were cut in halves. The cross section of each piece was observed and photographed by a Leica Stereomicroscope MZ12.5. The amount of root hairs that remained unhydrolyzed in each of the pieces of hide determined the amount of hydrogen peroxide to be used in the formulations of the pilot plant tests.

2.2.2. Pilot plant tests

When hydrogen peroxide is in contact with the hide at high pH values, both the hair and the collagen get hydrolyzed. This hydrolysis decreases the values of the physical properties of the leather while it increases its capacity for absorbing chromium (Morera et al., 2006).

First, laboratory tests determined the amount of hydrogen peroxide needed for conducting an effective unhairing (Section 2.2.1.). Our objective was then to find out the influence of the length of the oxidative unhairing on the physical properties and chrome absorption of the final leather as well as the values of certain parameters in wastewater floats resulting from unhairing and tanning. We must consider that not all leathers are

expected have the same properties. These depend on the final leather goods intended to be manufactured. It is by all means important to determine the minimum time possible for the oxidative unhairing to work, since the greater the hydrolysis of hair and hide, the higher the pollutant loads in the effluents. This parameter is also extremely significant because it will determine the amount of chromium salt to be added in subsequent tanning operations. Adding too much chromium salt leads to higher concentrations of chromium in wastewaters, which is not only detrimental to the environment, but also raises water treatment costs.

To perform the test a first reductive unhairing was performed on three soaked and fleshed hides, following the formulation shown in Table 1. Subsequently, each hide was divided in four symmetric pieces.

Then one piece was separated from each hide. An oxidative unhairing, with an offer of 3% hydrogen peroxide, was carried out for each of the remaining pieces. This amount was chosen based on the results of the laboratory tests (Section 2.2.1.). The rotating time was different for each of the tests performed: 2 hours, 4 hours and 6 hours respectively.

The formula being used is shown in Table 4, which includes the chemical operation performed immediately afterwards, known as bating. The aim of bating is to hydrolyze the proteins called elastins to get softer hides. In our case the bating was very soft (because the hydrogen peroxide hydrolyzes the collagen more that the sodium sulfide does).

Table 4

Pilot plant tests: Oxidative unhairing formula

30% Water	T = 25 ºC
1% Sodium hydroxide (50%)	Rotate 30 min.; pH =13

1.5% Hydrogen peroxide (50%)	Rotate 15 min.
2% Sodium hydroxide (50%)	Rotate 15 min.
1.5% Hydrogen peroxide (50%)	Rotate 2 h., 4 h. or 6 h.; pH =11.2-11.4
1.5% Formic acid	In three times. Rotate 45 min.
170% Water	Rotate 6h. Night: Rotate 5 min. per hour.
	pH = 7.8
	Drain
200% Water	T = 30ºC
	Rotate 20 min.
	Drain
150% Water	T = 37ºC
0.1% Bating agent	Rotate 20 min.; pH = 8.5
Drain and wash	

To quantify improvements in the reductive-oxidative system versus the reductive system (already implemented on an industrial scale), the unhairing of the fourth piece of each hide was completed with a traditional reductive unhairing. The formula we used is shown in Table 5, which includes the chemical operations performed immediately afterwards: deliming and bating. Deliming was carried out in order to remove lime and alkaline products from within the skins or hides.

After bating, all the tested hides were collected, placed in the same drum and the process continued.

Table 5

Pilot plant tests: Reductive unhairing formula (second part)

200% Water	T = 30ºC

1% Sodium sulfide	
2% Lime	Rotate 6 h. Overnight rest
	Drain
200% Water	T = 30ºC
	Rotate 20 min.
	Drain
150% Water	T = 37ºC
0.3% Sodium metabisulfite	
1.5% Ammonium sulfate	Rotate 30 min.; pH = 8.5
1% Bating agent	Rotate 1 h.
Drain and wash	

The wastewaters resulting from all the unhairings were analyzed. We focused only on the effluents resulting from the second part of the unhairing, in which the hair root had been hydrolyzed, since the first unhairing stage is common for both systems under examination. Subsequently, the hides continued to be processed until they underwent the tannage with chromium salt. We then performed physical and chemical tests on the resulting leathers and final effluents to quantify the differences between the two systems.

2.2.3. Physical testing and chemical analysis

The parameters analyzed in the wastewaters from the unhairing operation were Chemical Oxygen Demand (COD), Suspended Solids (SS), Conductivity and sulfide content (S^{2-}).

Analyses of COD, SS and Conductivity were carried out according to the Standard Methods (APHA, 1998).

Sulfide content was determined through the Sulfide Test Kit, reference 114779, Merck brand, which is a photometric method.

Chromium oxide content in the tanning effluents was analyzed following the ASTM D-3898-93 standard, which is a test method for chromic oxide in basic chromium tanning liquors (ASTM, 2009).

The Official IUP and IUC methods specified below were followed to analyze the leather: *IUP 6 (ISO 3376:2011). Determination of tensile strength and percentage extension* (IUP 6, 2011); *IUP 8 (ISO 3377-2:2002). Determination of tear load - Part 2: Double edge tear* (IUP 8, 2002); *IUP 9 (ISO 3379:2015). Determination of distension and strength of surface (Ball burst method)* (IUP 9, 2015); *IUP 16 (ISO 3380:2015). Determination of shrinkage temperature up to 100 ºC* (IUP 16, 2015) and *IUC 8-1 (ISO 5398-1:2007). Chemical determination of chromic oxide content. Part I: Quantification by titration* (IUC 8-1, 2007).

3. Results and discussion

3.1. Laboratory tests

Fig. 3 shows the cross section of the hide after the reductive unhairing was performed. Numerous remains of hair were clearly visible. The addition of hydrogen peroxide led to the removal of these hair remains. It was necessary to add 3% hydrogen

peroxide to virtually achieve complete removal. Likewise, it was observed that the hydrogen peroxide bleaches the hair before hydrolyzing it completely. This actually constitutes an advantage for the tanner because even if traces of hair remain, if they are colorless, they do not detract from the quality of the leather as the final color of the product is not affected. However, if the hair remains are black, which sometimes occurs when applying traditional reductive unhairing, small black spots usually appear, resulting in leather that may lack the desired evenness and color brightness. Figs. 4 and 5 show cross sections of two hides unhaired with 1% and 3% hydrogen peroxide. The hide unhaired with 1% hydrogen peroxide clearly shows remains of hair that are yet to be hydrolyzed, while the hide unhaired with 3% hydrogen peroxide shows that hydrolysis is almost complete. Only tiny remains may be appreciated in the form of different colors dots.

Considering that hydrogen peroxide hydrolyzes not only keratin but also collagen, it was concluded that the 3% hydrogen peroxide offer was most fit for the types of hides used in the tests. This offer enabled a sufficient degree of unhairing of the hides, while sustaining a minimal degradation of the collagen, that is to say, it preserved the physical properties of the hide. It is important to note that this amount was valid for the hides used in the experiments described, but may vary depending on the type of hides. The more similar the hides being used are to the ones being used in the tests, the more the ideal offer will approach 3%. It stands to reason that if one wants to unhair cattle hides the ideal percentage of hydrogen peroxide will be closer to 3% than if one intends to unhair goatskins, for example. Nor should we forget that the offer of unhairing chemicals is traditionally measured on hide weight but should really be measured in relation to hide yield, since what really matters is the amount of hair contained in the hide, not the total amount of hair and collagen. It is also commonly known that black hair is harder to remove than white hair, for

example. Therefore, within cattle hides, the ideal percentage of hydrogen peroxide may vary depending on factors including animal breed and hair color.

3.2 Pilot plant tests

After performing the different unhairings, the cross sections of the hides were observed through the lens. Fig. 6 shows the appearance of the hide after the second unhairing, in this case using sodium sulfide to hydrolyze the hair. Figs. 7, 8, and 9 show the appearance of the skin after the second unhairing, using in this case hydrogen peroxide as unhairing agent with different rotating times (2 hours, 4 hours and 6 hours). The second reductive unhairing hydrolyzes virtually all the hair but in Fig. 6 remains of black hair are still observed. These remains may damage the final appearance of the leather, especially if the desired item requires light color unfinished leather. Fig. 7, 8 and 9 outline two conclusions. The first is that with 3% hydrogen peroxide and after 2 hours of unhairing, the hair remains are already decolored, evolving from black to yellow. The second is that the longer the unhairing time, the more the hair remains are effectively hydrolyzed.

The results of the analyses of unhairing and tanning effluents as well as the physical and chemical tests of the final leather are shown in Table 6.

Table 6

Pilot plant tests: Results of comparative analyses

Type of unhairing (second part)		Oxidative		Reductive
Time (h)	6	4	2	
Wastewater analyses				
Conductivity (mS/cm)	6.85±0.34	6.66±0.33	7.33±0.37	9.86±0.49

SS (kg/t hide)	2.35±0.12	1.56±0.07	1.89±0.10	6.36±0.32
COD (kg/t hide)	16.97±0.34	12.83±0.23	11.00±0.23	11.28±0.21
Sulfide (kg HS^-/t hide)	0	0	0	1.0±0.1
Leather analyses				
Chromium of leather (% Cr_2O_3)	3.45±0.02	3.38±0.02	3.28±0.02	3.14±0.02
Shrinkage temperature (ºC)	112±1	113±1	112±1	107±1
Tensile strength (N/mm^2)	1313±28	1502±30	1882±41	2323±44
% Elongation	63.2±2.4	63.7±2.6	66.2±2.5	69.4±2.8
Tearing Load (N/mm)	99.3±6.0	113.3±6.8	127.9±7.7	146.8±8.8
Grain Crack Load (N)	57±3	57±3	49±3	40±2
Grain Crack Distension (mm)	12.03±0.30	11.55±0.29	11.86±0.30	12.55±0.31

The results of the analyses of the unhairing effluents suggest the conclusions set out below. The conductivity of the unhairing effluent decreases dramatically (between 26% and 32%) when replacing sodium sulfide and calcium hydroxide with hydrogen peroxide and sodium hydroxide. This is reasonable since in the first case (sodium sulfide and calcium hydroxide unhairing) more salts are formed than in the second case (hydrogen peroxide and sodium hydroxide unhairing), in which hydrogen peroxide is transformed into water. Suspended solids show a similar behavior towards conductivity, decreasing between 63% and 75% when using oxidative unhairing versus reductive unhairing. The presence of excess calcium hydroxide (very insoluble) in the reductive unhairing may explain this decline. The rise in suspended solids when increasing unhairing time using hydrogen peroxide is probably due to a greater partial hydrolysis of the hair and the collagen. Regarding the chemical oxygen demand, it is found that when the oxidative unhairing takes 2 hours, the results are practically the same as those obtained through reductive unhairing.

By increasing the time of the oxidative unhairing, COD rises up to 50%. This increase is due to a greater hydrolysis of collagen, which raises the organic matter in the float. It is also noteworthy that in oxidative unhairing, sulfide content is not detected, which is reasonable, as no sodium sulfide has been used in the process. In contrast, in reductive unhairing sulfide does indeed appear in the effluents. The presence of sulfide involves increased risks to workers due to its toxicity. Also, it raises the toxicity parameter of wastewaters, which in turn increments treatment costs. During wastewater treatment sulfides are oxidized to sulfates, a new source of problems within the treatment process. Finally, it is interesting to note that in the oxidative unhairing the role of acid formic is not only to decrease pH of medium. It also acts as a deliming chemical. Therefore the addition of ammonium compounds is avoided, which is very good from environmental point of view.

The results of the chemical and physical analyses to which the final leather was subjected enable us to reach the conclusions set out below. The hides that underwent oxidative unhairing absorbed higher amounts of chrome (between 4% and 10% rises) than those that underwent reductive unhairing. According to some authors (Shi et al., 2003) this is probably due to increase of carboxyl groups derived from oxidation of aminoacid residues containing hydroxyl groups thus serine and threonine residues. Chromium mainly coordinates with collagen by forming links with carboxylic groups. When the duration of the oxidative unhairing increases, the oxidative effect is boosted; thus the number of carboxylic groups rise and, consequently, more chrome is absorbed. The chromium content in the leather affects its physical properties. Actually, if the leather absorbs an excess of chromium its overall quality may even be damaged. In oxidative unhairing a smaller offer of chromium salt is needed to get the same amount of chromium absorption as in reductive unhairing, which implies that the chromium content of the effluent, and therefore its

pollution load, will be smaller. This constitutes an economic advantage because it involves both less spending on the chromium salt needed for tanning and less spending on wastewater treatment. The shrinkage temperature depends on the amount of chromium coordinated with the collagen. Leathers unhaired through oxidative unhairing show higher shrinkage temperatures than those unhaired through reductive unhairing. It must be noted that the three pieces of leathers unhaired with hydrogen peroxide show exactly the same shrinkage temperatures, which suggests that once a certain point has been reached more absorption of chromium does not contribute to increasing the degree of tanning (resistance to collagen degradation) of the leather. Tensile strength, elongation and tear strength follow the trends described above. The values obtained by the leathers unhaired using hydrogen peroxide are lower than those obtained by the leathers unhaired using sodium sulfide. The longer the oxidative unhairing, the lower the tensile strength values. The most significant changes occur in the tensile strength values, with decreases ranging from 19% to 43%. Tear strength values show more moderate falls, between 13% and 33%. The decrease in elongation values is even more moderate, between 4% and 9%. The greater hydrolysis of collagen is probably the main reason for the decrease in these physical properties. The measurement of the distension and strength of the grain by the ball burst test shows that a stronger force (between 21% and 42%) must be applied to break the grain (the upper and most valued part of the hide) in hides subjected to oxidative unhairing versus those subjected to reductive unhairing. Besides, the longer the oxidative process, the greater the strength to be applied in order to break the grain. In contrast, the distension is slightly higher in the hides subjected to reductive unhairing (between 4% and 5%). This shows that the longer the oxidative process, the greater the distension.

From the overall results, it can be concluded that with a two-hour oxidative unhairing the leathers obtained show similar chemical and physical characteristics to the leathers unhaired through reductive unhairing. Besides, much less contamination is generated in the wastewater, especially in conductivity (26% decrease), suspended solids (75% decrease) and sulfides (100% decrease). If the time of oxidative unhairing increases, the physical properties of the leather deteriorate, the COD increases, and conductivity and SS in wastewater decrease. Also, the amount of chromium contained in the leather increases 4%. Therefore, chromium salt offer in the tannage may be reduced and, consequently, the amount of chromium present in the effluents resulting from the tannage may also decrease.

Therefore, our research suggests that oxidative unhairing enables to obtain similar quality leathers while significantly decreasing the pollution being discharged into wastewaters. Oxidative unhairing also allows for an easier use of the solid waste generated (sulfide-free fleshings).

3.3. Economic considerations

As it is less pollutant, oxidative unhairing presents economic advantages in terms of cost of wastewater treatment (unhairing and tanning) and solid waste management (fleshings without the presence of sulfides). From the commercial viewpoint, no problems are observed, since the final leather shows similar or even better quality (depending on the final product) than the final leather obtained following the traditional unhairing process.

At this point though, it is imperative to compare the costs of the two unhairing systems to ensure that the proposed system is feasible on an industrial scale. This may be calculated by simply comparing the costs of the reagents used in each process, since the

other factors (water consumption, rotating time, among others) are virtually the same in both systems. This comparison is shown in Table 7. The costs in the calculations were supplied by a distributor of chemicals and are representative of those currently being applied in Spain.

Table 7

Economic viability study

Unhairing type	Chemical	t chemical /t hide	Price (€/t chemical)	Cost (€/t hide)
Reductive	Sodium sulfide	0.1	870	87
	Lime	0.2	150	30
	Sodium hydrogen sulfite	0.03	480	14.4
	Ammonium sulfate	0.18	310	55.8
	Bating agent	0.1	900	90
	TOTAL COST			***277.2***
Oxidative	Sodium hydroxide	0.3	240	72
	Hydrogen peroxide	0.3	360	108
	Formic acid	0.15	620	93
	Bating agent	0.01	900	9
	TOTAL COST			***282***

The cost difference in the chemicals of both unhairing processes is 0.48 € / t of hide, that is, 1.73%. The calculation includes the chemicals used in the deliming and bating

operations, which are both post-unhairing. After these operations the hides, regardless of the type of unhairing employed, undergo the same process. The calculation does not include the hypothetical chromium salt savings in oxidative unhairing, as these have not been experimentally tested.

This minimal difference in cost is more than offset by the savings in treatment costs involved in decreasing the pollution load of the resulting wastewater. Therefore, we can state that the process is economically viable. Even in countries where the discharge of highly polluted wastewater is not penalized, the cost difference is so small that it should not prevent the implementation of the new unhairing system.

4. Conclusions

Traditional unhairing has been significantly modified, replacing part of the sodium sulfide with hydrogen peroxide as unhairing agent. This change is economically viable and has allowed a significant reduction of the pollution load and toxicity of the wastewater as well as a minimization of the solid waste resulting from the unhairing process. Actually, the sustainability of the whole process has not only been improved environmentally but also from the perspective of the safety and health of workers, as the possibility of producing hydrogen sulfide during the process is eliminated with the new system.

References

Andrioli, E., Gutterres, M., 2014. Associated use of enzymes and hydrogen peroxide for cowhide hair removal. J. Am. Leather Chem. As. 109, 41-48.

APHA, 1998. Standard Methods for the Examination of Water and Wastewater, 18th. ed. American Public Health Association, Washington DC.

ASTM, 2009. ASTM D3898-93: Standard test method for chromic oxide in basic chromium tanning liquors, ASTM International Database. http://www.astm.org (accessed January 2015)

Bayramoglu, E.E., Yorgancioglu, A., Yeldiyar, G., Onez, E., 2014. Extraction of keratin from unhairing wastes of goatskin and creating new emulsion formulation containing keratin and calendula flower (*calendula officinalis L.*). J. Am. Leather Chem. As. 109, 49-55.

Black, M., Canova, M., Rydin, S., Scalet, B.M., S. Roudier, S., Sancho, L.D., 2013. Best Available Techniques (BAT) Reference Document on for the Tanning of Hides and Skin, p. 46. European Commission Database. http://eippcb.jrc.ec.europa.eu/reference/BREF/TAN_Published_def.pdf (accessed January 2015).

Bronco, S., Castiello, D., d'Elia, G., Salvadori, M., Seggiani, M. Vitolo, S., 2005. Oxidative unhairing with hydrogen peroxide: development of an industrial scale process for high-quality upper leather. J. Am. Leather Chem. As. 100, 45–53.

Castiello, D., Puccinu, M., Seggiani, M., Vitolo, S., Zammori, F., 2008. Life cycle assessment (LCA) of the oxidative unhairing process by hydrogen peroxide. J. Am. Leather Chem. As. 103, 1–6.

Dettmer, A., Cavalli, E., Ayub, M.A.Z., Gutterres, M., 2012. Optimization of the unhairing leather processing with enzymes and the evaluation of inter-fibrillary proteins removal: an environment-friendly alternative. Bioprocess Biosyst. Eng. 35, 1317–1324.

FAO, 2013. Market and Policy Analyses of Raw Materials, Horticulture and Tropical Products Team. World Statistical Compendium for raw hides and skins, leather and leather footwear 1993-2012. Food and Agricultural Organization (FAO) Database. http://www.fao.org/fileadmin/templates/est/COMM_MARKETS_MONITORING/Hides_Skins/Documents/COMPENDIUM2013.pdf (accessed January 2015).

Frendrup, W., 2000. United Nations Industrial Development Organization Database. http://www.unido.org/fileadmin/user_media/Publications/Pub_free/Hair_save_unhairing_methods_in_leather_processing.pdf (accessed January 2015).

Galarza, B.C., Cabello, I., Greco, C.A., Hours, R., Schuldt, M.M., Cantera, C.S., 2010. Alternative technologies for adding value to bovine hair waste. J. Soc. Leather Tech. Ch. 94, 26-32.

Haydar, S., Aziz, J.A., 2009. Characterization and treatability studies of tannery wastewater using chemically enhanced primary treatment (CEPT) – A case study of Saddiq Leather Works. J. Hazard. Mater. 163, 1076-1083.

Heidemann, E., 1993. Fundamentals of Leather Manufacturing, first ed. Eduard Roether, K.G., Darmstadt (Germany), p. 189.

IUC 8-1, 2007. ISO 5398-1:2007. Leather - Chemical determination of chromic oxide content - Part 1: Quantification by titration.

IULTCS, 2008. IUE- 6: Pollution values from tannery processes under conditions of good practice. International Union of Leather Technologists and Chemists (IULTCS) Database. http://www.iultcs.org/pdf/IUE6_2008.pdf (accessed January 2015).

IUP 6, 2011. ISO 3376:2011. Leather - Physical and mechanical tests - Determination of tensile strength and percentage extension.

IUP 8, 2002. ISO 3377-2:2002. Leather - Physical and mechanical tests - Determination of tear load - Part 2: Double edge tear.

IUP 9, 2015. ISO 3379: 2015. Leather - Determination of distension and strength of surface (Ball burst method).

IUP 16, 2015. ISO 3380:2015. Leather - Physical and mechanical tests - Determination of shrinkage temperature up to 100 °C.

Jian, S., Wenyi, T., Wuyong, C., 2011. Kinetics of enzymatic unhairing by protease in leather industry. J. Clean. Prod. 19, 325–331.

Kanagaraj, J., Senthilvelan, T., Panda, R.C., Kavitha, S., 2015. Eco-friendly waste management strategies for greener environment towards sustainable development in leather. J. Clean. Prod. 89, 1-17.

Morera, J.M., Bartolí, E., Borras, M.D., Banaszak, S., 2006. Oxidative unhairing of leathers: influence of several process parameters and environmental improvements. J. Am. Leather Chem. As. 101, 347–354.

Morera, J.M., Bacardit, A., Ollé, L., Bartolí, E., Borras, M.D., 2008. Minimization of the environmental impact in the unhairing of bovine hides. Chemosphere 72, 1681–1686.

Saravanabhan, S., Thanikaivelan, P., Rao, J.R., Nair, B.U., Ramasami, T., 2006. Reversing the conventional leather processing sequence for cleaner leather production. Environ. Sci. Technol. 40, 1069–1075.

Sengil, A., Kulaç, S., Özakar, M., 2009. Treatment of tannery liming drum wastewater by electrocoagulation, J. Hazard. Mater. 167, 940-946.

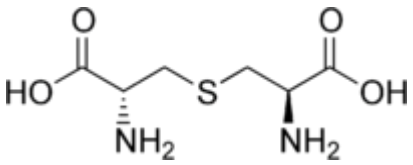
Shi, B., Lu, X., Sun, D., 2003. Further investigations of oxidative unhairing using hydrogen peroxide, J. Am. Leather Chem. As. 98, 185–192.

Thangam, E.B., Nagarajan, T., Rajkumar, G.S., Chandrababu, N.K., 2001. Application of alkaline protease isolated from *Alcaligenes faecalis* for enzymatic unhairing in tanneries. J. Am. Leather Chem. As. 96, 127–132.

Valeika, V., Baleska, K., Valeikiene, V., Kolodzeiskis, V., 2009. An approach to cleaner production: from hair burning to hair saving using a lime-free unhairing system, J. Clean. Prod. 17, 214-221.

Vidal, G., Nieto, J., Cooman, K., Gajardo, M., Bornhardt, C., 2004. Unhairing effluents treated by an activated sludge system. J. Hazard. Mater. 112, 143-149.

Figure 1



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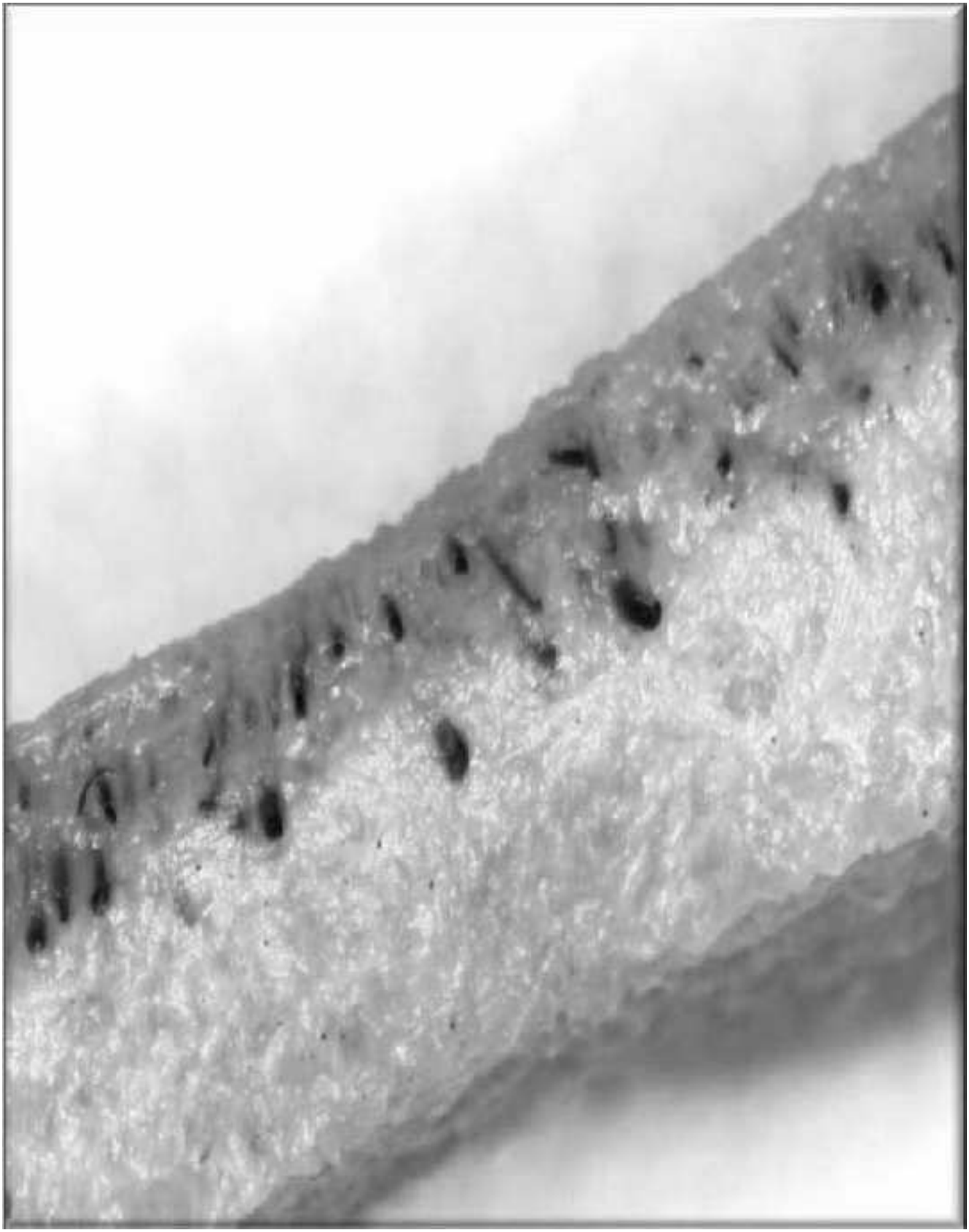

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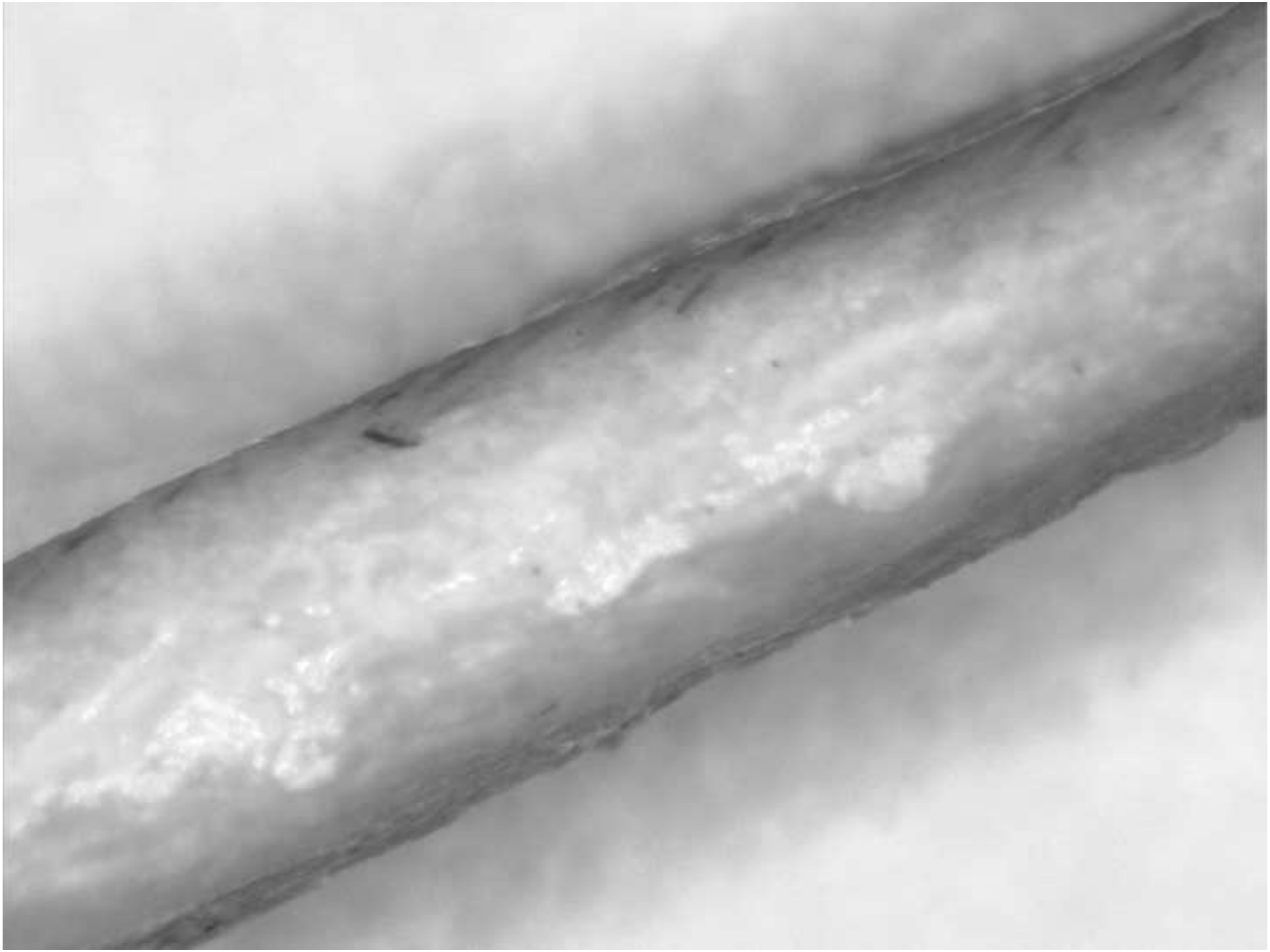

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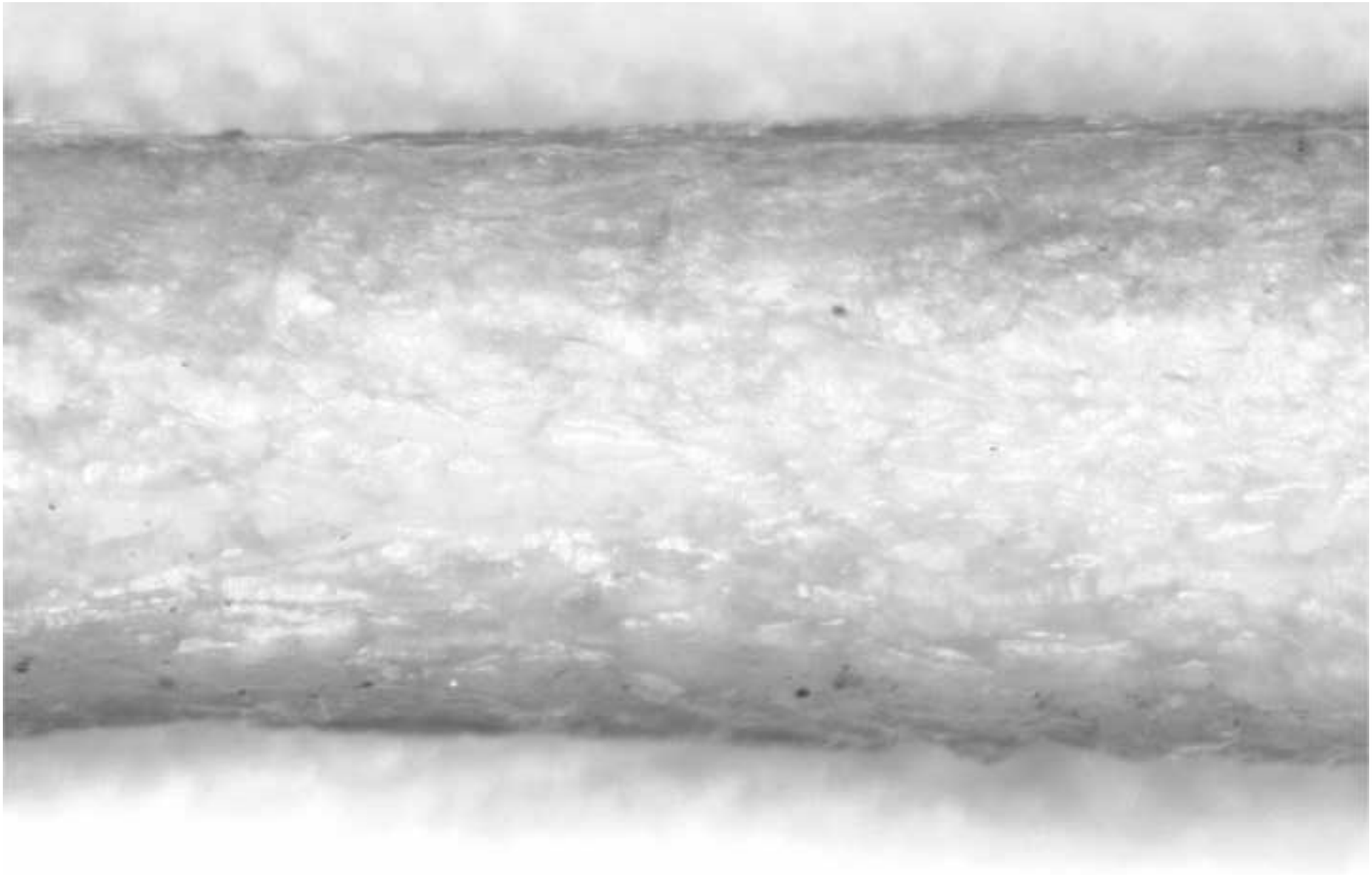

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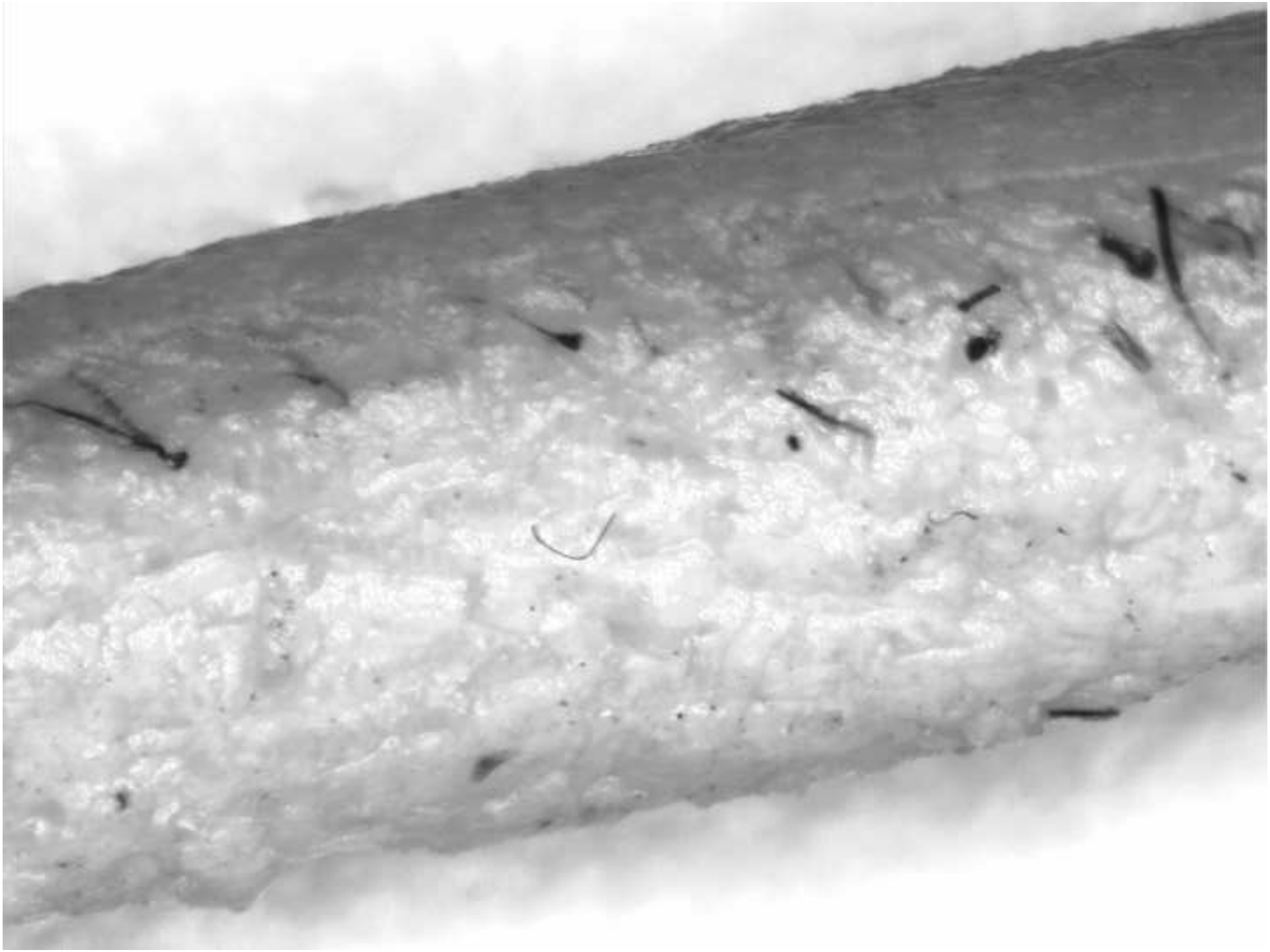

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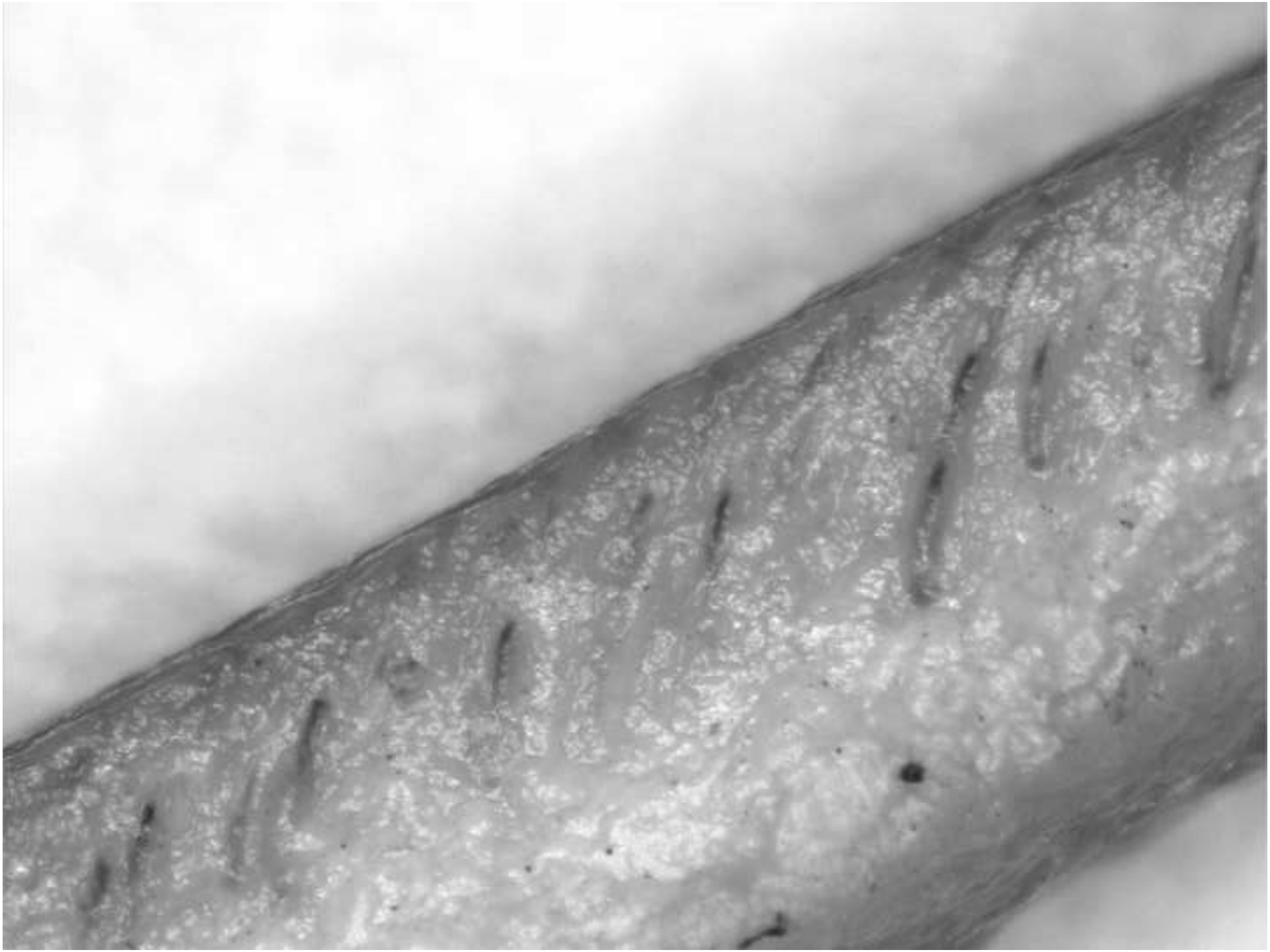

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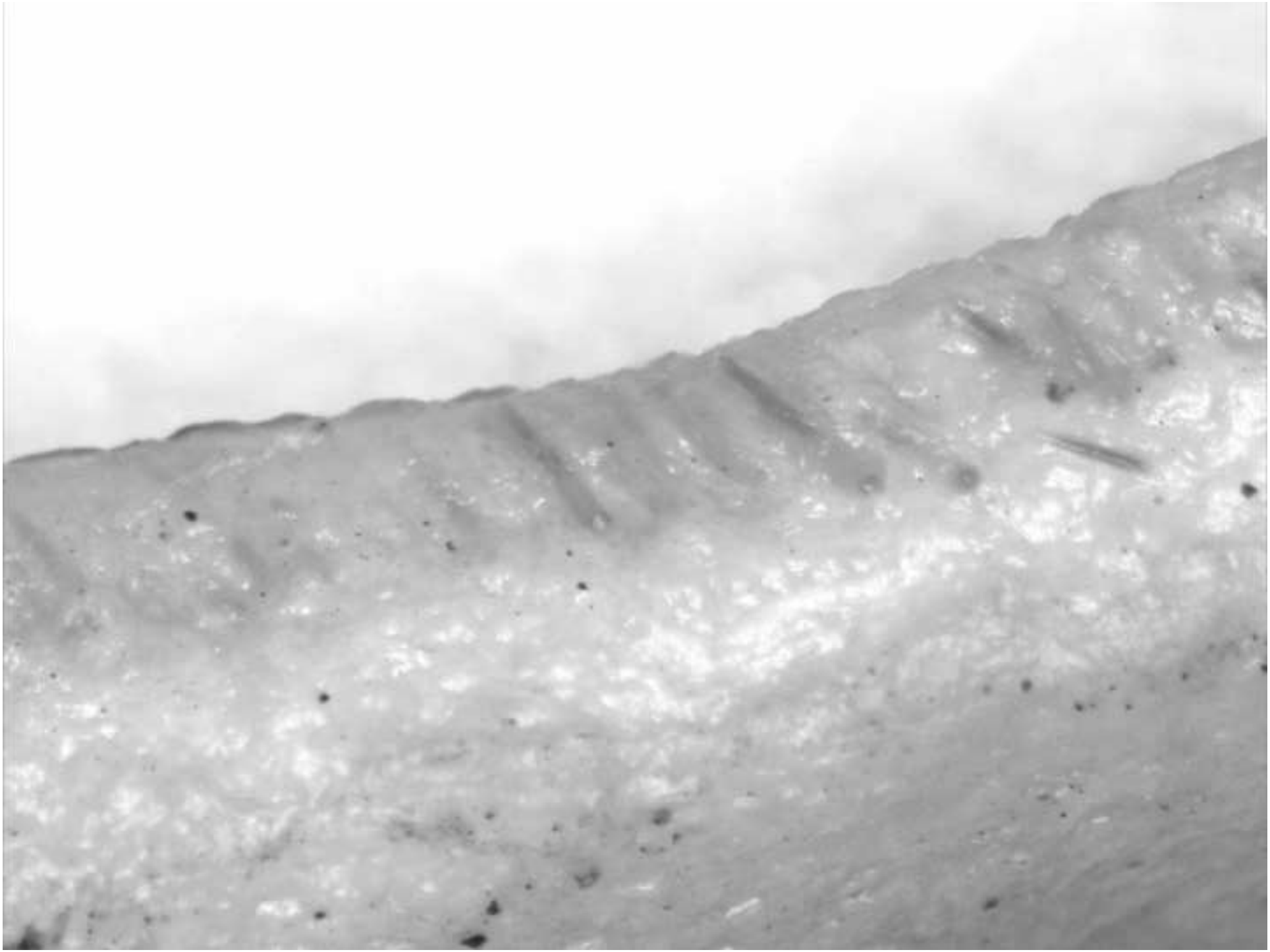

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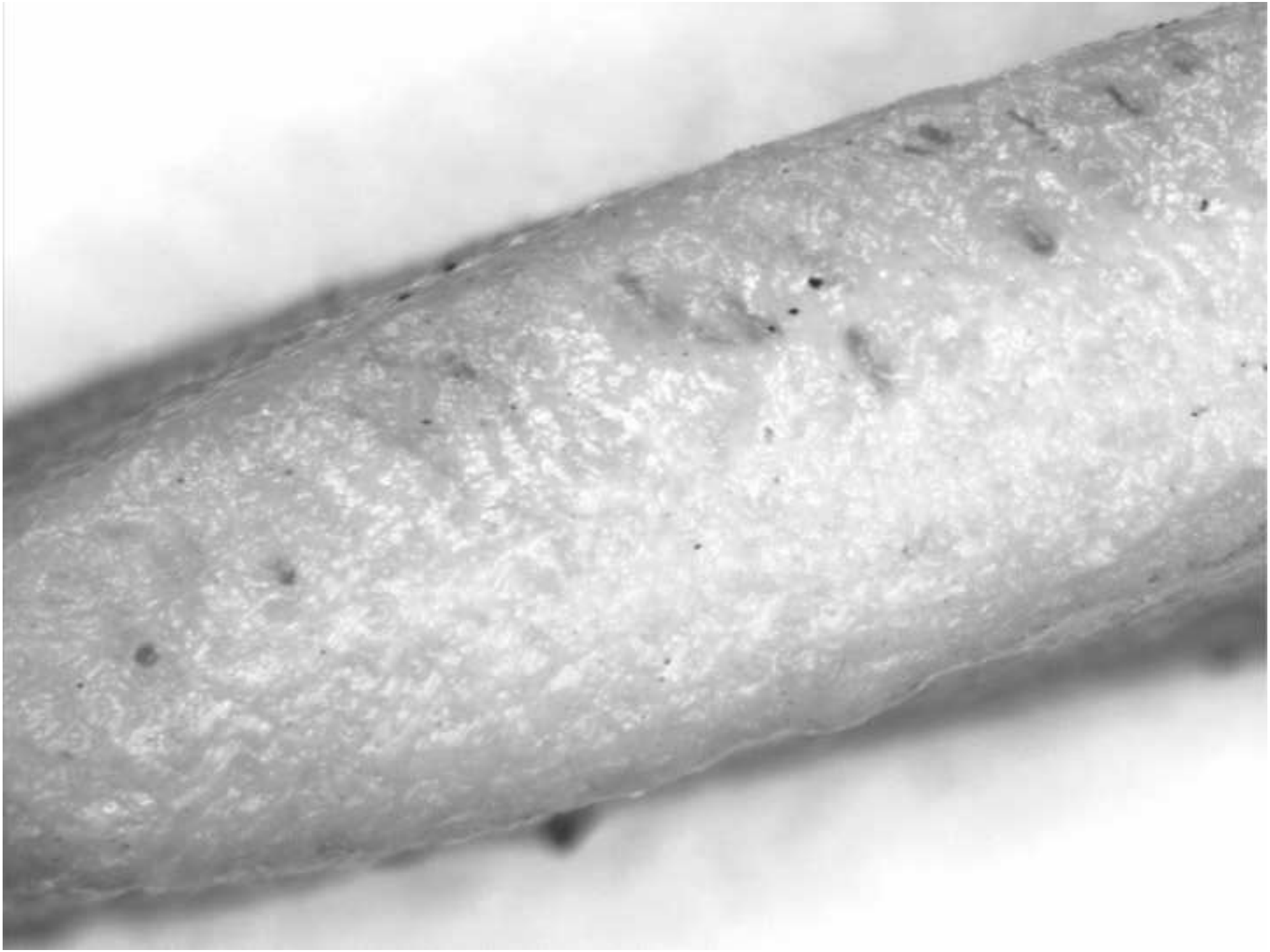

Captions

Fig. 1. Lanthionine structure.

Fig. 2. Pilot plant drum.

Fig. 3. Laboratory tests. Enlarged view (12.5x) of the cross section of the hide after reductive unhairing.

Fig. 4. Laboratory tests. Enlarged view (12.5x) of the cross section of the hide unhaired with 1% hydrogen peroxide.

Fig. 5. Laboratory tests. Enlarged view (12.5x) of the cross section of the hide unhaired with 3% hydrogen peroxide.

Fig. 6. Pilot plant tests. Enlarged view (12.5x) of the cross section of the hide unhaired with sodium sulfide and lime.

Fig. 7. Pilot plant tests. Enlarged view (12.5x) of the cross section of the hide unhaired with hydrogen peroxide for 2 hours.

Fig. 8. Pilot plant tests. Enlarged view (12.5x) of the cross section of the hide unhaired with hydrogen peroxide for 4 hours.

Fig. 9. Pilot plant tests. Enlarged view (12.5x) of the cross section of the hide unhaired with hydrogen peroxide for 6 hours.

ABSTRACT

This study aims to diminish the pollution being discharged into wastewaters through changes in the unhairing process. To this aim, we are replacing a reductive hair degrading process with a process which combines a reductive hair degrading process with an oxidative hair degrading process. Hydrogen peroxide is used to decrease the supply of sulfide as unhairing chemical. As a result, commercially acceptable leather regarding both costs and quality is obtained and significant reductions in the contaminant load of the wastewater being discharged are observed. Results indicate that wastewater conductivity is cut by 26%, suspended solids decrease by 75%, observable sulfide disappears, while the amount of chromium being absorbed by the hides is increased. This leads to considerable savings in the chromium salt offer in hide tanning and, consequently, a decrease in the amount chromium in the wastewater.